

O.Z. 6339-WO

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Method for the production of HSiCl_3 by catalytic hydrodehalogenation of SiCl_4

The invention relates to a process for the catalytic hydrodehalogenation of silicon tetrachloride (SiCl_4) to form trichlorosilane (HSiCl_3) in the presence of hydrogen.

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In many industrial processes in silicon chemistry, SiCl_4 and SiHCl_3 are formed together. It is therefore necessary to convert these products into one another and thus meet the respective demand for one of the products.

10 In addition, high-purity HSiCl_3 is an important starting material in the production of solar silicon.

EP 0 658 359 A2 discloses a process for the catalytic hydrodehalogenation of SiCl_4 to form HSiCl_3 in the presence of hydrogen, in which finely divided transition metals or
15 transition metal compounds selected from the group consisting of nickel, copper, iron, cobalt, molybdenum, palladium, platinum, rhenium, cerium and lanthanum are used as unsupported catalyst, with these being able to form silicides with elemental silicon or silicon compounds. Problems are, due to the strongly endothermic nature of the reaction, the indirect introduction of the heat of reaction and the sintering of the catalyst
20 particles associated with a loss in activity and difficulties in regulating the degree of conversion. In addition, the separation of the used finely divided catalyst from the product mixture requires a considerable outlay.

On this subject, I. Röver et al., "The catalytic hydrogenation of chlorosilanes – the
25 crucial print of production of electronic – grade silicon", Silicon for the Chemical Industry VI, Loen, Norway, June 17-21, 2002; Eds.: M. A. Øye et al., Trondheim, Norway, 2002, page 209 ff., report that not all transition metals are able to form silicides since silicide formation in the case of these elements is at least partially kinetically inhibited.

30 It was thus an object of the present invention to provide a further possible way of

preparing HSiCl_3 from SiCl_4 .

According to the invention, this object is achieved as set forth in the claims.

- 5 Thus, it has surprisingly been found that HSiCl_3 can be produced in a simple, economical and effective manner by catalytic hydrodehalogenation of SiCl_4 in the presence of hydrogen when a gaseous feed mixture comprising hydrogen and silicon tetrachloride is brought into direct contact with at least one hot heating element of a resistance heating device, with the heating element being composed of a metal suitable
10 for this purpose or a metal alloy.

It is particularly surprising that heating elements comprising tungsten, niobium, tantalum or corresponding alloys display catalytic activity under the present reaction conditions, although this would not have been expected because of the kinetic inhibition of silicide
15 formation.

In addition, such heating elements have mechanical stability and the removal of finely divided catalyst dust can advantageously be dispensed with.

- 20 A further advantage is that the energy required for the present reaction can be introduced directly via the resistance heating device and energy losses due to indirect heating of the reactor can thus advantageously be avoided.

Thus, conversion into HSiCl_3 in the vicinity of the thermodynamic conversion can
25 advantageously be obtained according to the invention when an SiCl_4/H_2 mixture is passed over the heated elements of a resistance heating device. In the present process, it is also possible to obtain the product composition desired in the particular case quickly and flexibly by variation of the electric power applied to the heating elements of the resistance heating device. The energy consumption is significantly

lower than in the case of conventional indirect heating since, advantageously, only the gas in the vicinity of the also catalytically active heating element rather than all the gas stream is brought to the reaction temperature.

- 5 The present invention accordingly provides a process for the catalytic hydrodehalogenation of SiCl_4 to form HSiCl_3 , which comprises bringing a gaseous feed mixture comprising hydrogen and silicon tetrachloride into direct contact with at least one heating element of a resistance heating device, with the heating element being composed of a metal or a metal alloy and being heated to carry out the reaction.

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In the process of the invention, use is made of, in particular, at least one heating element composed of a metal from the group consisting of niobium, tantalum and tungsten or of a metal alloy comprising niobium, tantalum and/or tungsten, in the case of which silicide formation is substantially inhibited under the reaction conditions.

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Thus, the process of the invention is preferably carried out using at least one heating element which has the form of a wire, a spiral, a web, a tube, e.g. tubes which may have webs or are provided with crosses or inserts or whose walls are provided with holes, a plate, for example smooth or corrugated plates, perforated plates or plates having folds, creases or raised regions or packets of plates, a mesh, for example smooth or

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corrugated meshes, or a honeycomb body, for example with a round, square, triangular, hexagonal or octagonal cell cross section.

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Preference is given to heating elements whose wire diameter, wall thickness or plate or layer thickness is from 0.1 mm to 10 mm, preferably from 0.3 to 8 mm, particularly preferably from 0.5 to 5 mm.

Such heating elements of a resistance heating device known per se are, in the case of the process of the invention, preferably used in a flow reactor which can be supplied

with a gaseous H_2/SiCl_4 mixture. The heating elements described are generally commercially available and are advantageously provided with water-cooled electric power connections in a manner known per se. To carry out the process of the invention, electric power is supplied to the resistance heating device present, as a result of which the heating elements are heated and the hydrodehalogenation of SiCl_4 to form HSiCl_3 takes place according to the invention. The electric power is generally increased slowly, for example over a period of about 30 minutes, until the desired reaction temperature has been reached. To regulate and control heating, temperature measurements are preferably carried out at the heating elements, at the reactor wall and in the feed stream or product stream.

In the process of the invention, the heating elements of the resistance heating device are preferably operated at a temperature in the range from 300 to 1250°C, in particular from 700 to 950°C.

The reaction according to the invention is thus appropriately carried out at a temperature in the range from 600 to 950°C, in particular from 700 to 900°C, and a pressure of from 0.1 to 100 bar abs., preferably from 1 to 10 bar abs., in particular from 1.5 to 2.5 bar abs.

In the process of the invention, the reaction is preferably carried out at a space velocity ($\text{SV} = \text{volume flow}/\text{reactor volume provided with heating elements}$) of from 2000 to 750 000 h^{-1} , preferably from 5000 to 500 000 h^{-1} , and/or a volume flow based on catalyst surface area ($\text{AV} = \text{volume flow}/\text{catalyst surface area}$) of from 10 to 0.01 m/s, particularly preferably from 1 to 0.05 m/s. Furthermore, preference is given to passing the gas mixture of hydrogen and silicon tetrachloride over the heating elements of the resistance heating device at a linear velocity ($\text{LV} = \text{volume flow}/\text{cross-sectional area of reactor}$) of from 0.01 to 10 m/s, preferably from 0.01 to 8 m/s, particularly preferably from 0.02 to 5 m/s. The volume flows on which the reaction kinetic parameters indicated

above and below are based are in each case at STP. The process parameters are advantageously set so that laminar flow occurs.

5 The process of the invention is carried out using a gaseous SiCl_4/H_2 mixture which preferably has a molar $\text{SiCl}_4:\text{H}_2$ ratio of from 1:0.9 to 1:20, particularly preferably from 1:1 to 1:10, very particularly preferably from 1:1.5 to 1:8, in particular from 1:2 to 1:4.

10 In general, the SiCl_4 is, if necessary, brought into the gas phase and a defined amount of hydrogen gas is metered into it. Here, traces of water and oxygen, in particular, have to be excluded. It is advantageous to use pure to very pure SiCl_4 and hydrogen.

15 The desired degree of conversion $[\text{conv.} = 100\% \cdot c(\text{HSiCl}_3)/c_0(\text{SiCl}_4)]$ can advantageously be regulated or set in the process of the invention by setting the electric power of the resistance heating device without interruption of the process becoming necessary.

20 Furthermore, the reaction according to the invention is appropriately carried out in a flow reactor whose walls or wall insides are composed of niobium, tungsten, tantalum, a niobium-, tungsten- and/or tantalum-containing alloy, a heat-resistant glass, in particular fused silica, a heat-resistant glaze or a heat-resistant ceramic or specialty ceramic.

25 The product mixture or product gas stream obtained in the process of the invention can advantageously be passed through at least one heat exchanger located at the beginning of the process, i.e. upstream of the reactor, in order to vaporize SiCl_4 and/or preheat the H_2/SiCl_4 -containing feed mixture so as to save energy before the product mixture/gas stream is processed further or worked up. In this way, the feed gas stream and the product gas stream can advantageously be conveyed in countercurrent in order to preheat the feed gas and thus achieve particularly energy-efficient operation.

In the process of the invention, the reaction product, i.e. product mixture, obtained in this way can be worked up or processed further, preferably by (i) fractionating or at least partially condensing the product mixture in a manner known per se to give liquid, advantageously highly pure HSiCl_3 and recirculating any hydrogen and silicon tetrachloride obtained to the feed stream of the present process or (ii) passing the product stream as starting material to a direct further use, for example in an esterification with an alcohol to form alkoxysilanes, in a hydrosilylation process for converting olefins into organochlorosilanes, in the preparation of monosilane or solar silicon or in the preparation of pyrogenic silica.

In general, a defined mixture of hydrogen and silicon tetrachloride is prepared in order to carry out the process of the invention. A reactor which is resistant to silicon tetrachloride and HCl and relatively high temperatures and has metallic heating elements of a resistance heating device integrated into its reaction region is usually firstly baked and flushed with dry inert gas, for example argon, or with hydrogen. After electric power has been connected, the resistance heating device can be run up, set to the reaction temperature and supplied with the feed gas mixture of H_2 and SiCl_4 . At the outflow end of the reactor, a product mixture which advantageously comprises HSiCl_3 up to the concentration corresponding to the thermodynamic equilibrium is obtained.

The present invention is illustrated by the following examples without the subject matter of the present invention being restricted thereby.

Examples:

Example 1

In a fused silica reactor having a diameter of 15 mm and a length of 250 mm, a W wire having a diameter of 0.4 mm and a length of 400 mm in the form of a spiral is used as

direct resistance heating device. This wire is heated to the reaction temperature of 800°C by application of a voltage of from 10 to 11 V. The temperature of the wire is measured by means of a sheathed thermocouple. A H_2/SiCl_4 mixture flows through the reactor at a throughput of 7 l/h. The conversion in the reaction is monitored by gas chromatography. Table 1 shows the conversion of SiCl_4 into HSiCl_3 at various H_2/SiCl_4 ratios.

Table 1

$n(\text{H}_2)/n(\text{SiCl}_4)$	Degree of conversion into HSiCl_3 (%)
4	15.3
5.5	18.3
6	19.0

10 **Example 2**

The apparatus described in example 1 is used. The degrees of conversion are determined as a function of the flow rate at 800°C and a constant $n(\text{H}_2)/n(\text{SiCl}_4)$ ratio of 6:1, cf. Table 2.

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Table 2

Volume flow at STP (l/h)	Degree of conversion into HSiCl_3 (%)
7	19.0
10.5	17.6
14	16.7

Example 3

5 In a fused silica reactor having a diameter of 15 mm and a length of 250 mm, a W wire having a surface area of 5.6 cm^2 is used in the form of a spiral. This wire is heated to the reaction temperature of 900°C by application of a voltage. A H_2/SiCl_4 mixture flows through the reactor at a throughput of 7 l/h. The conversion in the reaction is monitored by gas chromatography. Table 3 shows the conversion of SiCl_4 into HSiCl_3 at various H_2/SiCl_4 ratios.

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Table 3

$n(\text{H}_2)/n(\text{SiCl}_4)$	Degree of conversion into HSiCl_3 (%)
4	20.9
6	21.1

Example 4

15 The apparatus described in example 3 is used. It is operated at a constant molar H_2/SiCl_4 ratio of 6 and a throughput of 7 l/h. The electric power applied is increased from 65 W to 80 W. Within a few minutes, the degree of conversion has increased from 21.1 mol% to 23.4 mol%.